

Theoretical Study of Structure of Alkali Metal Cyanates and Isocyanates and Their Related Ion Pair S_N2 Reactions

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ABSTRACT: The structure of lithium and sodium cyanates and isocyanates and their related ion pair S_N2 reactions were investigated using molecular quantum mechanics at the Hartree–Fock (HF)/6-31G**//HF/6-31G** level. Extensive further calculations of some of the lithium systems at higher levels gave no significant changes in relative properties. The isocyanate ion pairs are the most stable monomeric forms. The lowest energy dimers are planar eight-membered rings. For the ionic S_N2 reaction of cyanate ion and methyl fluoride and chloride, methyl isocyanate is the predicted major product. The monomer ion pair inversion mechanism is predicted to preferentially form methyl cyanate but the calculations also indicate that reaction with dimeric ion pairs have no clear preference for forming methyl cyanate or isocyanate. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1325–1336, 1998

Keywords: cyanate; isocyanate; ambident; ion pair; S_N2 reaction

Introduction

Isocyanates and cyanates are an important class of compounds that have found a large variety of applications in organic, bioorganic, and polymer chemistry.¹ Organic isocyanates are commonly

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prepared from phosgenation of amines, imines, carbamates, and ureas. Rearrangements via nitrene intermediates are also often applied in their syntheses. On the other hand, the generally less stable cyanates are usually prepared from thermolysis of thiazotriazoles or reactions of alcohols with cyanogen halides. Unlike their thio derivatives, the most direct strategy of reacting organic halides with inorganic cyanate salts is not a practical route for the synthesis of organic isocyanates and cyanates.

Many studies have been done on the structures and reactivities of thiocyanates.² However, there

has been much less work done with cyanates and isocyanates. In 1978, Poppinger and Radom treated the lithium and methyl compounds together with other derivatives.³ More recently, McAllister and Tidwell studied a number of isocyanates with larger basis sets,⁴ and Schultz et al. computed cyanate ion and its alkali metal salts.⁵ In the present study, the reactions of some alkali metal cyanates with methyl fluoride and chloride are investigated by *ab initio* calculations. Due to the ambident nature of these nucleophiles, cyanate or isocyanate reacting with alkyl halide can produce either the corresponding alkyl isocyanate or alkyl cyanate and, accordingly, provides an opportunity to compare ionic and ion pair S_N2 reactions. Structures and energies were computed for monomers and dimers using consistent basis sets and were compared in the transition structures of ionic and ion pair S_N2 reactions. Our previous theoretical studies showed important differences between ionic and ion pair S_N2 reactions⁶; in the present work, these differences were extended to an ambident nucleophile.

Computational Methods

All geometries were fully optimized at the restricted Hartree-Fock level by using standard basis sets (3-21G* and 6-31G**) incorporated in the Gaussian-92⁷ and -94⁸ programs. Only 6-31G** values are discussed.⁹ Stationary points were characterized by frequency calculations. Additional calculations with limited sets of structures were also done at RHF/6-31 + G**, MP2¹⁰(full)/6-31 + G**//RHF/6-31 + G**, B3LYP¹¹/6-31 + G**//RHF/6-31 + G**, and B3LYP/6-31 + G**//B3LYP/6-31 + G**. There is little change in the general trend with the larger bases although energy differences among some isomers are reduced at the DFT level. Accordingly, for consistency between the lithium and sodium systems, the discussion makes use primarily of the 6-31G** results. Charges were computed by the Natural Population Analysis.¹² Cartesian coordinates of significant structures are available from the authors by request.

STRUCTURES OF ALKALI METAL CYANATES AND ALKALI METAL ISOCYANATES

A number of experimental IR studies of alkali metal cyanates in polar aprotic solution suggest the coexistence of free ions and contact ion pairs in

solution.¹³ The few theoretical studies available for pseudohalides have focused mainly on thio-cyanates.^{3-5,14} The linear monomeric lithium and sodium cyanates have been found to be the minimum energy forms.^{14a} Higher aggregates of cyanates were largely ignored in these studies, although they may be important in nonpolar solutions.

In this work, lithium and sodium were chosen as the cations. Because the number of possible isomers increases greatly with higher aggregation, detailed study was performed only up to dimers (Tables I and II and Figs. 1-3).

In general, isomers with more Li—N or Na—N bonds are more stable than those with more Li—O or Na—O bonds. Structurally, the metal—N bonds are 0.1–0.2 Å longer than the metal—O bonds.

For monomers, our results are similar to those of Veszprémi et al. for the pseudohalides.^{14a} However, their focus was on the π -complex monomers **20** and **21**, which are higher in energy than the isocyanate monomers **1** and **10**, but lower in energy than cyanate monomers **2** and **11**. In our calculations, lithium isocyanate monomer **1** is 11.44 kcal mol⁻¹ more stable than the cyanate monomer **2** at RHF/6-31G**. Meanwhile, sodium isocyanate monomer **10** is 10.11 kcal mol⁻¹ more stable than cyanate monomer **11**. Based on our calculations and others for the monomers, linear isocyanates are more stable than cyanates in the gas phase.

For dimers, there are seven different possible arrangements depending on the relative orientations of the OCN group and the ring size with the cations. In both lithium and sodium dimers, the eight-membered ring isomers are the minimum energy forms. This type of structure has been observed in many transition metal dimers with cyanate as a bridging ligand.¹⁵ Although the energy differences between the two eight-membered ring isomers are small (less than 1 kcal mol⁻¹), the head-to-tail dimers **6** and **15** were found to be consistently lower in energy than the head-to-head dimers **7** and **16**.

Square planar and six-membered ring dimers are at least 4 kcal mol⁻¹ higher in energy than the

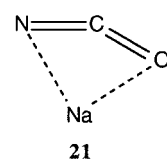
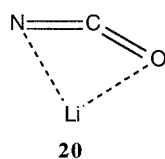


TABLE I. Absolute Energies (Hartree) and Relative Stability (kcal mol⁻¹) of Lithium Cyanates and Isocyanates

Cyanates or isocyanates	Energy (E) (Hartree)	RHF / 6-31G**			MP2(full) / 6-31 + G** //			B3LYP / 6-31 + G** //		
		ZPE (Hartree)	Relative energy ^{b,d} (kcal mol ⁻¹)	Dimerization energy ^c (kcal mol ⁻¹)	Relative energy ^b (kcal mol ⁻¹)	Dimerization energy ^c (kcal mol ⁻¹)	Relative energy ^b (kcal mol ⁻¹)	Dimerization energy ^c (kcal mol ⁻¹)	Relative energy ^{b,m} (kcal mol ⁻¹)	Dimerization energy ^c (kcal mol ⁻¹)
Monomer 1	-174.68692	0.01438	0	—	0 ^g	—	0 ⁱ	—	0 ^k	—
Monomer 2	-174.68823	0.01388	11.44	—	11.77	—	13.46	—	13.08	—
Dimer 3	-349.46069	0.03137	4.26	-53.03	1.85	-51.94	0	-51.25	0.16	-49.78
Dimer 4	-349.41955	0.03035	29.50	-27.78	27.27	-26.52	31.05	-20.20	30.28	-19.66
Dimer 5	-349.44066	0.03089	16.56	-40.73	14.09	-39.69	15.14	-36.11	14.86	-35.08
Dimer 6	-349.46750	0.03139	0	-57.28	0	-53.78	0	-51.25	0 ^l	-49.94
Dimer 7	-349.46590	0.03129	0.95	-56.34	1.02	-52.77	1.16	-50.09	1.07	-48.87
Dimer 8	-349.45830	0.03130	5.72	-51.56	3.79	-49.99	3.82	-47.43	3.63	-46.32
Dimer 9	-349.43793	0.03074	18.19	-39.10	15.76	-38.03	18.89	-32.35	18.25	-31.69
Cyanate anion 19	-167.19544	0.01187								

^a No imaginary frequencies were found in all of the above stationary points. ^b Energy relative to the minimum energy form in the same aggregation state. ^c Dimerization energies are calculated from the best monomeric state 1. ^d Including ZPE (scaled by 0.9). ^e Energy = -174.69656 h, ZPE = 0.01447 h. ^f Energy = -349.47681 h, ZPE = 0.03124 h. ^g Energy = -175.18309 h. ^h Energy = -350.45189 h. ⁱ Energy = -175.66764 h. ^j Energy = -351.41695 h. ^k Energy = -175.66970 h, ZPE = 0.01338 h. ^l Energy = -351.42126 h, ZPE = 0.02902 h. ^m Including ZPE.

TABLE II. Absolute Energies (Hartree) and Relative Stability (kcal mol⁻¹) of Sodium Cyanates and Isocyanates

Cyanates or isocyanates	RHF / 6-31G**			
	Energy E (Hartree)	ZPE (Hartree)	Relative energy ^{b,d} (kcal mol ⁻¹)	Dimerization energy ^c (kcal mol ⁻¹)
Monomer 10	-329.07085	0.01336	0	—
Monomer 11	-329.05432	0.01290	10.11	—
Dimer 12	-658.22334	0.02841	4.42	-50.28
Dimer 13	-658.18812	0.02739	25.94	-28.75
Dimer 14	-658.20615	0.02792	14.93	-39.77
Dimer 15	-658.23032	0.02834	0	-54.70
Dimer 16	-658.22912	0.02829	0.72	-53.97
Dimer 17	-658.22361	0.02833	4.20	-50.49
Dimer 18	-658.20629	0.02775	14.74	-39.95

^a No imaginary frequencies were found in all of the above stationary points. ^b Energy relative to the minimum energy form in the same aggregation state. ^c Dimerization energies are calculated from the best monomeric state 10. ^d Including ZPE (scaled by 0.9).

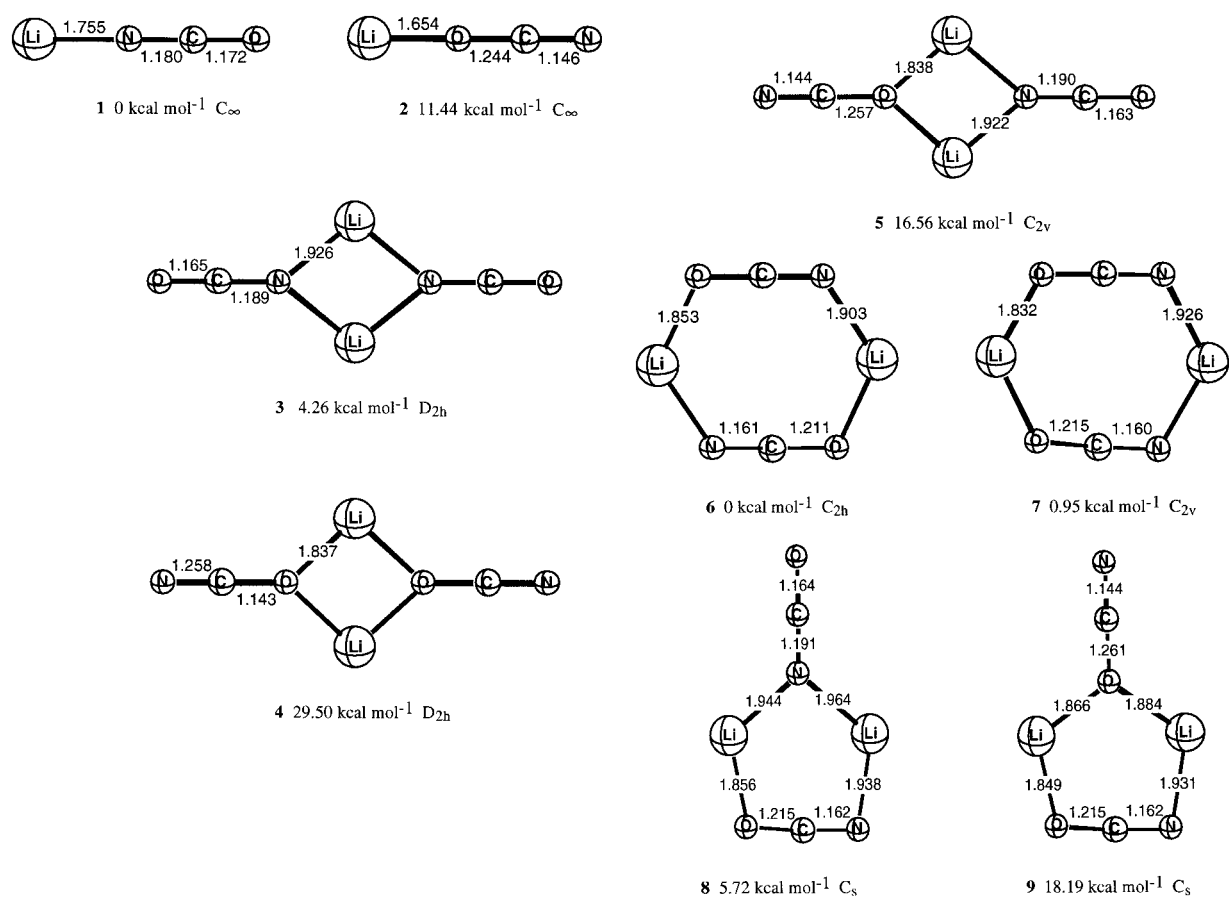


FIGURE 1. Structures and relative energies of lithium cyanates and isocyanates at RHF / 6-31G**.

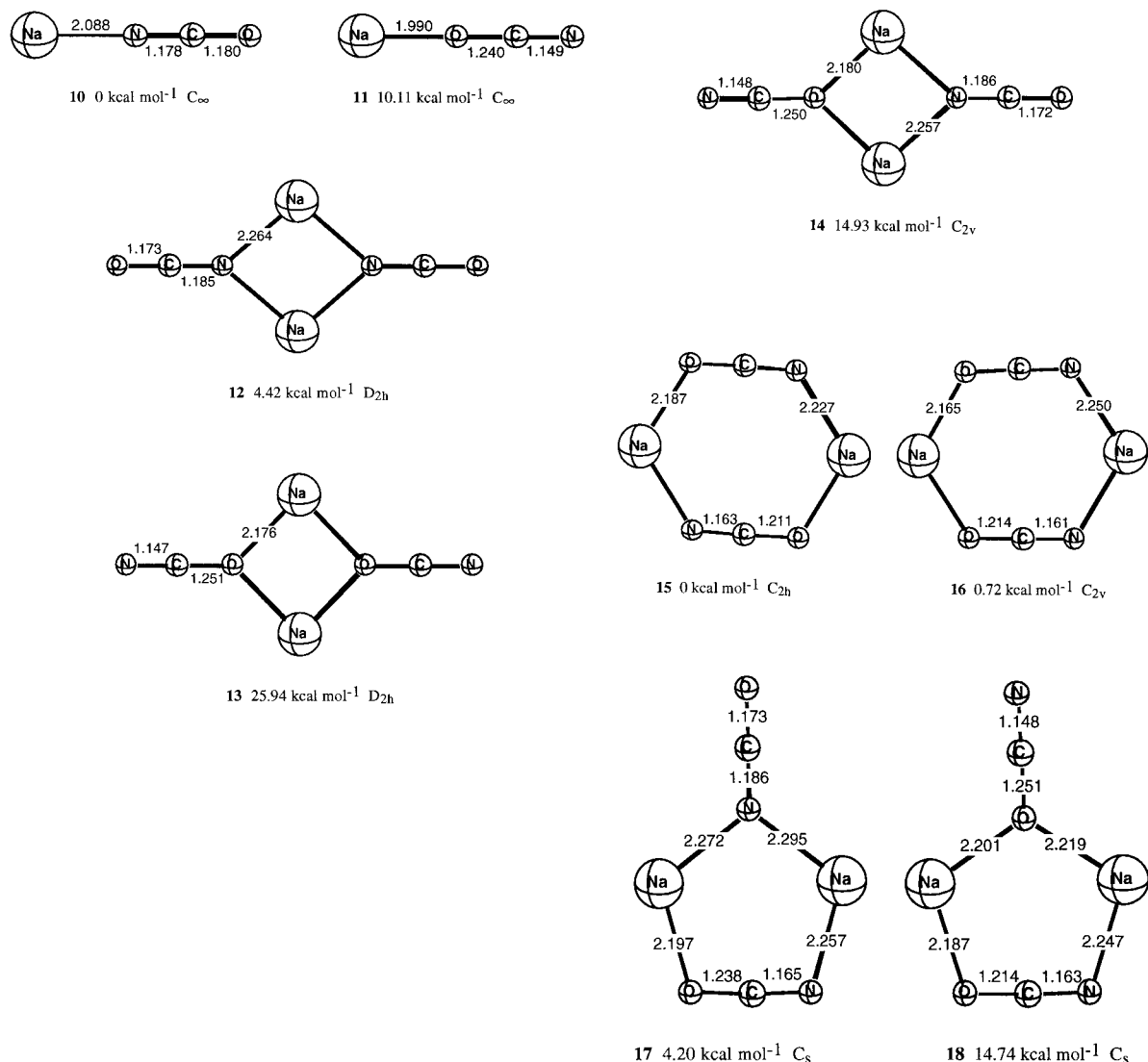
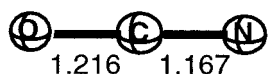


FIGURE 2. Structures and relative energies of sodium cyanates and isocyanates at RHF / 6-31G**.

most stable eight-membered ring dimers at RHF/6-31G**. This result clearly shows the importance of the eight-membered ring dimers, which are not generally considered in theoretical and experimental studies of ambident anion aggregates.



19 C_∞

FIGURE 3. Structure of cyanate ion at RHF / 6-31G**.

Dimerization energies were calculated by the formula:

$$E(\text{dimer}) - 2 \times E(\text{the most stable monomer}) = \text{Dimerization energy}$$

Dimerization is exothermic in the gas phase by 20–57 kcal mol⁻¹. Although solvation and entropy effects were not considered, these numbers are sufficiently large that aggregation is undoubtedly important in many solvents.

ION PAIR S_N2 REACTIONS

Because of problems of solubility and availability, only a few experimental studies of chemical

reactions of metal cyanates have been carried out. Nucleophilic substitution reactions of alkyl halides, tosylates, or sulfates with ionic cyanates generally yield only the corresponding alkyl isocyanates or the trimeric trialkyl isocyanurates.¹⁶ This extraordinary selectivity has been explained by isomerization [eq. (1)] of the first formed alkyl cyanates (methyl isocyanate is 25.0 kcal mol⁻¹ lower in energy than methyl cyanate at the RHF/6-31G** level).¹ The ambident nature of the ionic cyanates toward aliphatic carbon is thus neither proved nor disproved.



Our previous computational studies of ion pair S_N2 reactions showed some important differences from corresponding ionic systems⁶; hence, we have carried out a theoretical study of ion pair reactions of lithium and sodium cyanates to determine whether a related experimental study would be of interest. Results of our calculations are shown in Tables III and IV.

FREE ION REACTIONS

The experimental IR studies by Chabanel et al.¹³ found a mixture of free ions and ion pairs of lithium and sodium cyanates in DMSO and HMPA. If nucleophilic substitution is carried out in these aprotic polar solutions, products will undoubtedly come principally from the ionic mechanism, because free ions are generally more reactive than ion pairs.¹⁷ Indeed, a few reports do show that reactions of lithium or sodium cyanates and alkyl halides in highly polar solvents generate alkyl isocyanates.¹⁶ Theoretical calculations of ionic mechanisms provide some valuable insights in these reactions. Furthermore, these calculations are also essential for the comparison of the ionic with ion pair reactions.

Transition structures were found for the inversion mechanism (Fig. 4). Transition structure **23** is 7.9 kcal mol⁻¹ lower in energy than **22** for the reaction of cyanate ion and methyl fluoride at 6-31G**. For the reaction of cyanate ion and methyl chloride, transition structure **25** is 4.9 kcal mol⁻¹ lower in energy than **24** at 6-31G**. These results show a strong preference for nitrogen in the cyanate ion as the attacking site in the inversion pathway, which correlates very well with the experimental results. Additionally, the large energy gap between nitrogen and oxygen as the attacking site may be enough to explain the exclusive forma-

tion of alkyl isocyanates. Isomerization of the products may not be the cause of yielding only one product. Meanwhile, although the angles N—C—F and N—C—Cl are close to 180°, their inversion transition structures are not linear. The C—N—C angles are 160° in the reaction of methyl fluoride and 144° in the reaction of methyl chloride.

ION PAIR S_N2 REACTIONS OF MONOMERIC LITHIUM CYANATE WITH METHYL FLUORIDE AND METHYL CHLORIDE

Ion pair S_N2 reactions of alkali metal cyanates and alkyl halides have not previously been investigated either experimentally or theoretically. Theoretical data obtained in this study may provide some information useful for future experimental studies.

Four different transition structures (TS) were found for the inversion mechanism of the reaction of monomeric lithium cyanate and methyl fluoride (Fig. 5). Two of them (**26** and **27**) involve a planar six-membered ring structure that has one nucleophilic site (N or O) of the cyanate coordinating with lithium, and the other nucleophilic site (O or N) attacking methyl fluoride. These types of transition structure (type **A** TSs) usually involve an almost linear cyanate moiety. The bridging action of the Li cation causes a decrease of the N—C—F or O—C—F angles from 180° to 130°, which is much larger than that of the identity reaction of lithium fluoride and methyl fluoride (80°).⁶ The remaining two planar four-membered ring transition structures (**28** and **29**) (type **B** TSs) also have an almost linear cyanate moiety. The nucleophilic attacking site also bonds with the lithium cation in this type of TS. The angles N—C—F or O—C—F are about 80°, which are similar to that of the identity reaction of lithium fluoride and methyl fluoride.

For the reaction of monomeric lithium cyanate and methyl chloride, four analogous transition structures (**30–33**) were located for the inversion mechanism. The N—C—Cl or O—C—Cl angles are about 5–10° larger than those of the corresponding TSs in the reaction with methyl fluoride. Moreover, the cyanate moiety remains almost linear in these TSs.

Generally, type **A** TSs are lower in energy than type **B** TSs in the inversion pathway. The lowest energy transition structures (**26** and **30**) are those with oxygen as the attacking site for both the methyl fluoride and chloride reactions. Although

TABLE III. Absolute Energies (Hartree) and Reaction Barriers (kcal mol⁻¹) of Transition Structures 22 and 23, 26–29, and 42–57

	RHF / 6-31G**			RHF / 6-31 + G**			MP2(full) / 6-31 + G** // RHF / 6-31 + G**			B3LYP / 6-31 + G** // RHF / 6-31 + G**		
	Absolute energy (Hartree)	ZPE (Hartree)	Reaction barrier ^{b,c} (kcal mol ⁻¹)	Absolute energy (Hartree)	Reaction barrier ^{b,c} (kcal mol ⁻¹)	Absolute energy (Hartree)	Absolute energy (Hartree)	Reaction barrier ^b (kcal mol ⁻¹)	Absolute energy (Hartree)	Absolute energy (Hartree)	Reaction barrier ^b (kcal mol ⁻¹)	Reaction barrier ^b (kcal mol ⁻¹)
Free ion reaction NCO ⁻ + MeF												
TS 22 (O attack)	-306.16250	0.05339	45.28	-306.21163	34.53	-307.04517	-307.04517	25.02	-307.85371	-307.85371	24.22	
TS 23 (N attack)	-306.17529	0.05368	37.41	-306.22238	27.81	-307.05566	-307.05566	18.44	-307.86625	-307.86625	16.35	
Monomer reaction LiNCO + MeF												
TS 26 (opp. side O attack, A)	-313.66472	0.05704	39.18	-313.68030	41.03	-314.51239	-314.51239	34.48	-315.37230	-315.37230	31.16	
TS 27 (opp. side N attack, A)	-313.65703	0.05713	44.06	-313.67820	42.19	-314.51152	-314.51152	35.03	-315.37206	-315.37206	31.31	
TS 28 (same side O attack, B)	-313.62494	0.05375	62.29	-313.64597	60.90	-314.46542	-314.46542	63.96	-315.33093	-315.33093	57.12	
TS 29 (same side N attack, B)	-313.64472	0.05470	50.41	-313.66565	49.08	-314.48903	-314.48903	49.14	-315.35754	-315.35754	40.42	
Dimer reaction (LiNCO) ₂ + MeF												
TS 42 (10-membered ring a)	-488.46522	0.07357	26.41	-488.48432	26.13	-489.80601	-489.80601	18.91	-491.14111	-491.14111	18.93	
TS 43 (10-membered ring b)	-488.46598	0.07353	25.92	-488.48444	25.98	-489.80516	-489.80516	19.44	-491.14112	-491.14112	18.92	
TS 44 (10-membered ring c)	-488.46591	0.07349	25.94	-488.48421	26.10	-489.80596	-489.80596	18.94	-491.14195	-491.14195	18.40	
TS 45 (10-membered ring d)	-488.46429	0.07354	26.98	-488.48290	26.96	-489.80523	-489.80523	19.40	-491.14078	-491.14078	19.13	
TS 46 (8-membered ring a)	-488.43848	0.07325	43.01	-488.45771	42.61	-489.78155	-489.78155	34.26	-491.11316	-491.11316	36.46	
TS 47 (8-membered ring b)	-488.44162	0.07339	41.12	-488.46064	40.83	-489.78365	-489.78365	32.94	-491.11615	-491.11615	34.59	
TS 48 (8-membered ring c)	-488.46466	0.07378	26.89	-488.48312	26.94	-489.80696	-489.80696	18.31	-491.14387	-491.14387	17.19	
TS 49 (8-membered ring d)	-488.46288	0.07374	27.98	-488.48150	27.93	-489.80627	-489.80627	18.74	-491.14279	-491.14279	17.87	
TS 50 (8-membered ring e)	-488.45327	0.07379	34.04	-488.47143	34.29	-489.79749	-489.79749	24.25	-491.13256	-491.13256	24.29	
TS 51 (8-membered ring f)	-488.43327	0.07314	46.22	-488.45147	46.47	-489.77802	-489.77802	36.47	-491.10937	-491.10937	38.84	
TS 52 (8-membered ring g)	-488.42948	0.07262	48.30	-488.44760	48.58	-489.77548	-489.77548	38.06	-491.10769	-491.10769	39.90	
TS 53 (8-membered ring h)	-488.44994	0.07329	35.85 ^d	-488.46808	36.09	-489.79556	-489.79556	25.46	-491.13139	-491.13139	25.03	
TS 54 (6-membered ring a)	-488.42463	0.07327	51.77 ^d	-488.44439	51.04	-489.77221	-489.77221	40.12	-491.10450	-491.10450	41.90	
TS 55 (6-membered ring b)	-488.40353	0.07274	64.66	-488.42319	64.00	-489.75173	-489.75173	52.97	-491.07994	-491.07994	57.31	
TS 56 (6-membered ring c)	-488.42988	0.07339	48.49	-488.44905	48.12	-489.77914	-489.77914	35.77	-491.11128	-491.11128	37.64	
TS 57 (6-membered ring d)	-488.45016	0.07397	36.09	-488.46943	35.66	-489.79875	-489.79875	23.46	-491.13500	-491.13500	22.76	
MeF	-139.03974	0.04210	—	-139.04914	—	-139.38425	-139.38425	—	-139.75432	-139.75432	—	
MeNCO	-206.79594	0.05424	0 ^e	-206.80112	0 ^e	-207.42809	-207.42809	0 ^e	-207.99896	-207.99896	0 ^e	
MeOCN	-206.75641	0.05449	24.95 ^e	-206.76219	24.61 ^e	-207.38430	-207.38430	27.48 ^e	-207.95173	-207.95173	29.64 ^e	

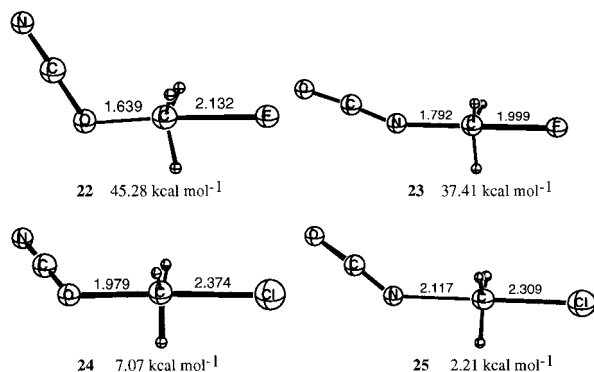
^a One imaginary frequency was found for all of the above transition structures unless stated otherwise. ^b Reaction barrier was calculated from the minimum energy form of the separated reactants. ^c Including ZPE (scaled by 0.9). ^d Two imaginary frequencies were found. ^e Energy relative to methyl isocyanate.

TABLE IV. Absolute Energies (Hartree) and Reaction Barriers (kcal mol⁻¹) of Transition Structures 24 and 25 and 30–41

	RHF / 6-31G**		
	Absolute energy (Hartree)	ZPE (Hartree)	Reaction barrier ^{b,c} (kcal mol ⁻¹)
Free ion reaction NCO ⁻ + MeCl			
TS 24 (O attack)	-666.28236	0.05258	7.07
TS 25 (N attack)	-666.29013	0.05260	2.21
Monomer reaction LiNCO + MeCl			
TS 30 (opp. side O attack, A)	-673.73963	0.05549	28.77
TS 31 (opp. side N attack, A)	-673.73607	0.05510	30.80
TS 32 (same side O attack, B)	-673.70116	0.05301	51.51
TS 33 (same side N attack, B)	-673.72351	0.05393	38.01
Monomer reaction NaNCO + MeF			
TS 34 (opp. side O attack, A)	-468.04721	0.05620	40.19
TS 35 (opp. side N attack, A)	-468.04521	0.05576	41.20
TS 36 (same side O attack, B)	-468.00029	0.05333	68.01
TS 37 (same side N attack, B)	-468.02138	0.05481	55.61
Monomer reaction NaNCO + MeCl			
TS 38 (opp. side O attack, A)	-828.13171	0.05465	23.76
TS 39 (opp. side N attack, A)	-828.12817	0.05419	25.72
TS 40 (same side O attack, B)	-828.09005	0.05265	48.77
TS 41 (same side N attack, B)	-828.11165	0.05420	36.09
MeCl	-499.09790	0.04038	—

^a One imaginary frequency was found for all of the above transition structures. ^b Reaction barrier was calculated from the minimum energy form of the separated reactants. ^c Including ZPE (scaled by 0.9).

the energy difference of the type **A** transition structures in the methyl chloride reaction is smaller than that of the methyl fluoride reaction, **30** is still clearly the best transition structure. These results indicate that alkyl cyanate should be the initial product for an inversion ion pair mechanism.

**FIGURE 4.** Transition structures and reaction barriers of the ionic S_N2 reactions at RHF / 6-31G**.

Previous reports have shown that introducing Li cation affects the ionicity of the ion pair reaction and increases the positive charge in the methyl group.⁶ This effect is also observed in our cases. NPA charges on the methyl group increase from +0.50 to +0.72 and from +0.52 to +0.69 for the methyl fluoride and methyl chloride reactions, respectively. However, the increase is not as large as in previous examples.

ION PAIR S_N2 REACTIONS OF MONOMERIC SODIUM CYANATE WITH METHYL FLUORIDE AND METHYL CHLORIDE

Transition structures for these systems are illustrated in Figure 6. Despite sharing similarities with the analogous lithium cyanate reactions, there are some general differences in these transition structures. Due to the increase in the size of the cation, the O(N)—C—F(Cl) angles in the type **A** TSs of the inversion pathway increase from ~135° to

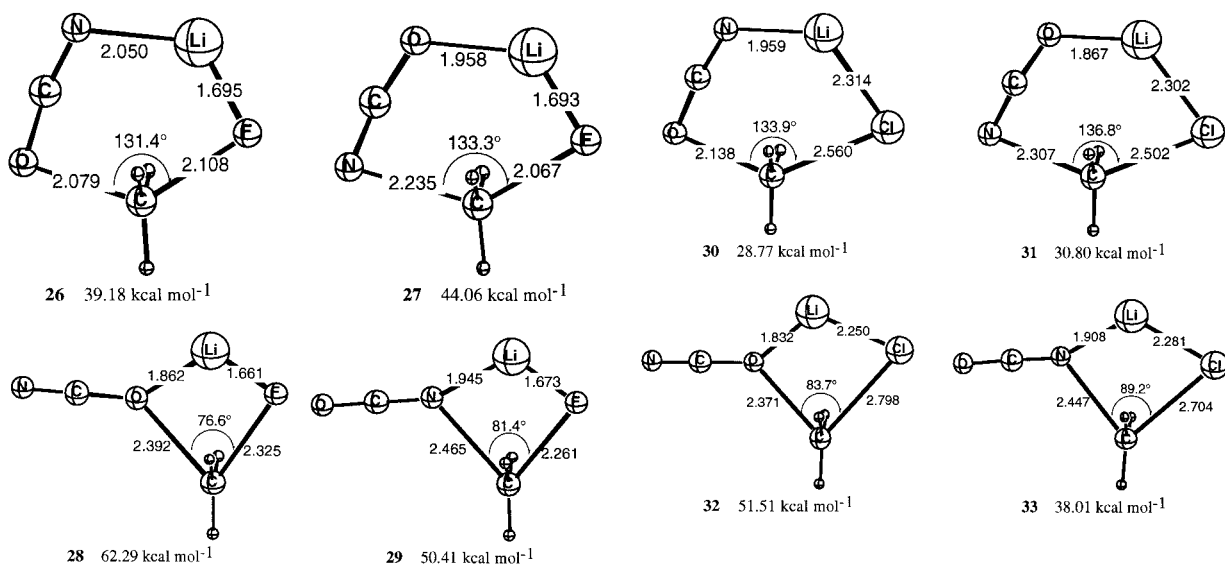


FIGURE 5. Transition structures and reaction barriers of ion pair S_N2 reactions of monomeric lithium cyanate and methyl fluoride or methyl chloride at RHF / 6-31G**.

~148°. For type **B** TSs of the inversion pathway, the same trend is found, but the changes are relatively small. Also, the cyanate moiety remains almost linear in all of the TSs.

In terms of reaction barriers, changing from Li to Na does not alter the general trend but does narrow the gaps between the transition structures. The best transition structures are **34** and **38**, which are of type **A** with oxygen as the attacking site. But the energy difference between the two type **A** TSs

is comparatively small (1.0 kcal mol⁻¹) in the methyl fluoride reaction. If the reaction goes through an ion pair inversion pathway, alkyl cyanate should still be the major initial product.

Including Na⁺ in the S_N2 reactions also leads to an increase in cationic character of the methyl group but the changes are only moderate. Increases in NPA charge from +0.50 to +0.64 in the methyl fluoride reaction and +0.52 to +0.62 in the methyl chloride reaction are observed. These

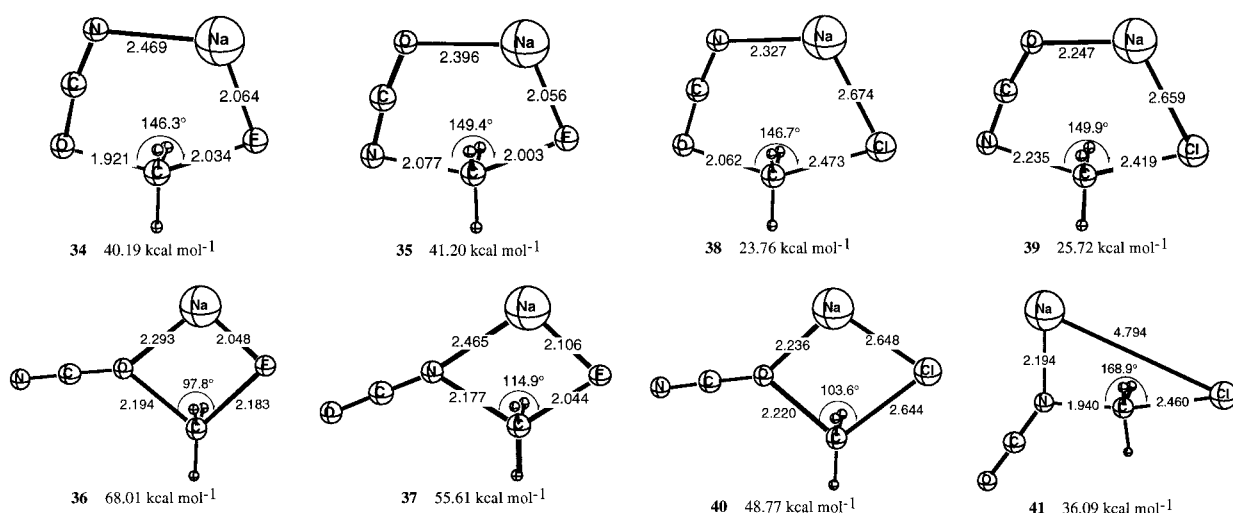


FIGURE 6. Transition structures and reaction barriers of ion pair S_N2 reactions of monomeric sodium cyanate and methyl fluoride or methyl chloride at RHF / 6-31G**.

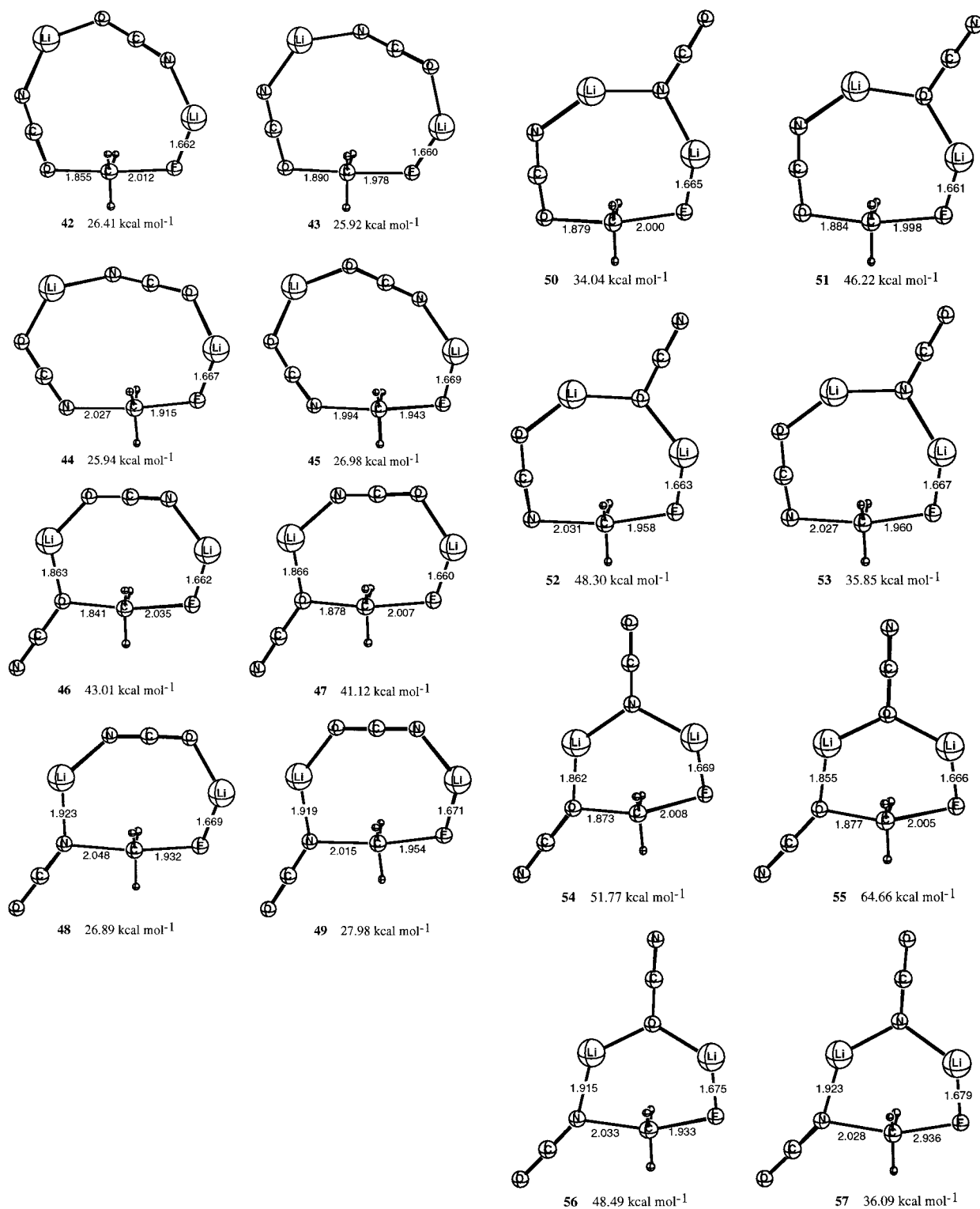


FIGURE 7. Transition structures and reaction barriers of inversion ion pair S_N2 reaction of dimeric lithium cyanate and methyl fluoride at RHF/6-31G**.

changes may be caused by the widening of the $\text{O(N)}-\text{C}-\text{F(Cl)}$ angles, thus leading to a more ionic $\text{S}_{\text{N}}2$ reaction character.

In summary, these calculations indicate that monomeric lithium and sodium cyanate ion pairs have a preference for forming cyanate rather than isocyanate products. To determine whether experimental $\text{S}_{\text{N}}2$ reactions in nonpolar solvents would be suggested as a route to alkyl cyanates, we next investigate the reactions of dimers, because such aggregates could also be important in nonpolar solvents.

INVERSION ION PAIR $\text{S}_{\text{N}}2$ REACTIONS OF DIMERIC LITHIUM CYANATE WITH METHYL FLUORIDE

Extending the study from monomers to dimers gives rise to a large increase in the number of possible transition structures. To save computer time, only the reaction of lithium cyanate and methyl fluoride with the more common inversion mechanism is examined. In the first part of this investigation, seven different dimers are found for lithium cyanate. Considering all possible arrangements, 16 transition structures for the inversion ion pair reaction of dimeric lithium cyanate and methyl fluoride are located and all contain a plane of symmetry (Fig. 7). The cyanate moiety is close to linear in all cases. Four of the 16 TSs involve a ten-membered ring structure. Eight contain an eight-membered ring and the remaining four are made up of six-membered rings. However, it should be pointed out that one kind of arrangement originating from the square planar dimer, that depicted in Figure 8, could not be found. Calculations start from these arrangements optimized to TS 50–53, which originate from the other kind of dimer structure (8 or 9).

One noteworthy feature of the dimeric TSs is that the $\text{O(N)}-\text{C}-\text{F}$ angles are much larger than those in monomeric TSs. Most are close to 170° . Incorporation of one more lithium cyanate moiety

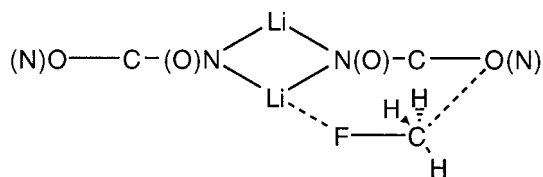


FIGURE 8. A possible structure, but not found as a transition structure, for the ion pair reaction of lithium cyanate dimer with methyl-fluoride.

leads to a relief of strain from the distortion of the preferred linear $\text{S}_{\text{N}}2$ attack. This is further confirmed by the population analysis of the TSs. NPA charges on the methyl group only increase from +0.5 to about +0.6. This result indicates that the dimeric aggregate TSs may be comparable to the free ion TSs.

There is no obvious trend for the reaction barriers of the dimeric TSs. In general, expansion of TSs ring size reduces the electronic energy of the TS more effectively. There are six transition structures with reaction barriers within $1.1 \text{ kcal mol}^{-1}$ of $26.9 \text{ kcal mol}^{-1}$, these include 42–45 and 48 and 49. Unfortunately, if displacement follows these TSs, a mixture of alkyl cyanate and isocyanate will result and the reactions in nonpolar media would then not be a useful route to alkyl cyanates. However, aggregates of lithium or sodium cyanate have not been observed experimentally. Furthermore, even if they exist, they may not be the reactive species in the ion pair $\text{S}_{\text{N}}2$ reaction. Also, entropy and solvation effects are not measured in this study, and could also play an important role. Nevertheless, the high calculated exothermicity of the dimerization of the metal cyanates in the gas phase and their lower reaction barriers are not encouraging in this regard.

Conclusions

Ab initio calculations on alkali metal cyanates have shown the energetic and structural differences of their monomeric and dimeric forms. Linear monomeric metal isocyanates are more stable than linear monomeric metal cyanates. A less commonly considered eight-membered ring isomer was found to be the lowest energy dimeric structure. Generally, lithium and sodium cations prefer to coordinate to the nitrogen of the cyanate in the dimeric aggregates.

A theoretical study has been reported on ionic, monomeric ion pair, and dimeric ion pair $\text{S}_{\text{N}}2$ reactions of metal cyanates and methyl halides. Methyl isocyanate was predicted to be the major product for the ionic reaction based on analyses of the transition structures. On the other hand, methyl cyanate should form preferentially if the reaction involves a monomer ion pair inversion mechanism. However, for dimer ion pair inversion pathways, a mixture of methyl isocyanate and cyanate has been predicted to result. This computational study suggests that experimental results with metal

cyanates in solvents of low polarity can be complex and not readily interpretable without extensive study of the actual reactive species. This study also emphasizes the importance of considering aggregates in such solvents.

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